

STUDY IN COMETARY ASTROPHYSICS

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Prepared by

Louis J. Stief & Vincent J. DeCarlo
Melpar, Inc.
3000 Arlington Boulevard
Falls Church, Virginia

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ABSTRACT

Studies have continued in the vacuum ultraviolet photolysis of hydrazine with an attempt to elucidate the primary photochemical process based on our previously reported spectroscopic observations and supplemented this quarter with product analysis. Ammonia, nitrogen, and hydrogen have been detected and the effect of pressure and wavelength on their formation has been examined.

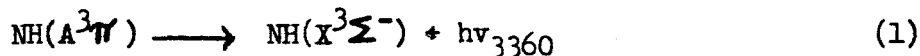
Conclusive evidence for CO and CO₂ formation in photolysis of CH₄-H₂O gaseous mixtures and in photolysis of the methane hydrate CH₄·6H₂O at -196°C has been obtained using isotopically labelled oxygen 18 water. The gas phase photolysis of C₂H₂-H₂O, C₂H₄-H₂O, and C₂H₆-H₂O have also been examined.

The construction of the proton source for the bombardment of low temperature solids has been completed.

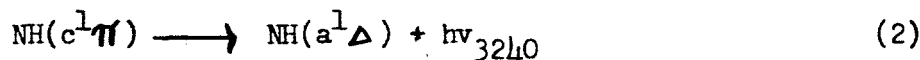
1. THE PRIMARY PHOTOCHEMICAL PROCESS IN THE VACUUM ULTRAVIOLET
PHOTOLYSIS OF HYDRAZINE

1.1 Introduction

Photolysis of hydrazine in the pressure region of 100 μ Hg at the Kr resonance lines (1165 $\overset{\circ}{\text{\AA}}$ and 1236 $\overset{\circ}{\text{\AA}}$) results in the observation of emission at 3360 $\overset{\circ}{\text{\AA}}$ corresponding to the transition



With continued photolysis, the NH emission at 3240 $\overset{\circ}{\text{\AA}}$ corresponding to the transition



begins to be observed. Since this emission is also observed in the vacuum ultraviolet photolysis of ammonia,¹ the accumulation of ammonia as a product of the photolysis of hydrazine is suggested. No emission is observed during photolysis of hydrazine at the Xe resonance lines (1470 $\overset{\circ}{\text{\AA}}$ and 1295 $\overset{\circ}{\text{\AA}}$). Since the submission of the previous quarterly report, a paper has appeared by Becker and Welge² on NH emission in the vacuum ultraviolet photolysis of N₂H₄ which corroborates our findings as previously reported. In an attempt to determine the primary photochemical process in the vacuum ultraviolet photolysis of hydrazine leading to the production of NH(A³ Π), the products of the reaction have been examined as a function of pressure and wavelength.

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1. K. H. Becker and K. H. Welge, Z. Naturforsch. 18a, 600 (1963).
 2. K. H. Becker and K. H. Welge, Z. Naturforsch. 19a, 1006 (1964).

1.2 Results

The only products detected in the photolysis of hydrazine are ammonia, nitrogen and hydrogen. The quantum yield (molecules of product formed per quantum of light absorbed) for these products as well as an estimate of the quantum yield for hydrazine disappearance have been determined (tables 1 and 2) in the micron pressure region and in the millimeter pressure region at both the Kr and Xe resonance lines.

Table 1

Effect of Pressure on the Quantum Yield (ϕ) of Product Formation and Hydrazine Disappearance in the Photolysis of Hydrazine at the Kr resonance lines (1236 μ and 1165 μ)

Pressure of Hydrazine	100 μ	1 to 3 mm
ϕ_{NH_3}	0.45 ± 0.05	1.0 ± 0.1
ϕ_{N_2}	0.45 ± 0.10	0.5 ± 0.05
ϕ_{H_2}	0.45 ± 0.10	1.0 ± 0.1
$\phi_{-\text{N}_2\text{H}_4}$	0.50 ± 0.05	~ 1

Table 2

Effect of Pressure on the Quantum Yield (ϕ) of Product Formation and Hydrazine Disappearance in the Photolysis of Hydrazine at the Xe Resonance Line (1470 μ)

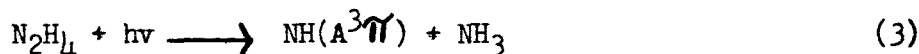
Pressure of Hydrazine	100 μ	150 μ	1 mm
ϕ_{NH_3}	0.2	0.30 ± 0.05	0.5
ϕ_{N_2}	0.3	0.48 ± 0.02	0.6
ϕ_{H_2}	0.4	0.58 ± 0.02	1.0
$\phi_{-\text{N}_2\text{H}_4}$	0.2	0.30 ± 0.05	~ 0.5

The effect of the duration of photolysis was examined at 100μ N_2H_4 for photolysis at the Kr lines and at 150μ N_2H_4 for photolysis at the Xe line. For photolysis at the Kr lines, the rate of production of all products and rate of disappearance of hydrazine are independent of time up to about 30% decomposition (photolysis time of about 5 minutes). Beyond this point, a steady state appears to be maintained wherein the pressure of NH_3 and pressure of N_2H_4 change very little with time. It is at this point also that ammonia and hydrazine are each absorbing 30% of the incident light. Evidently hydrazine is being photolyzed to produce ammonia and ammonia is being photolyzed to produce hydrazine. Consequently, the quantum yields quoted in table 1 have been determined at photolysis times such that the yields are independent of time. However, even at the shortest photolysis times at which measurable amounts of product could be obtained, significant photodecomposition of ammonia was probably occurring. Hence the ϕ_{NH_3} represent minimum values and, since photolysis of ammonia produces hydrazine, the values determined for $\phi_{-N_2H_4}$ also represent a minimum for hydrazine actually being removed by photolysis. Despite this consideration, ϕ_{NH_3} was the most reproducible quantity measured and did not appear to decrease with photolysis time for the experiments reported here. In the millimeter Hg pressure range, the percent decomposition is of course smaller and subsequent photolysis of products is negligibly small. The quantum yield for hydrazine disappearance is however only approximate in this range since the change in pressure is small. The relative absorption coefficients of N_2H_4 and

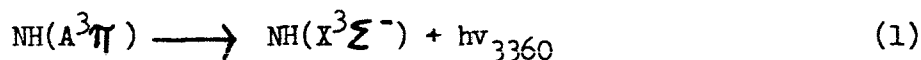
NH_3 at 1470\AA are such that product photolysis is not a problem even for the low pressure experiments. In general, the results for 1470\AA photolysis are more reproducible and no effect of the duration of the photolysis on the quantum yields was observed for up to 30% decomposition.

1.3 Discussion

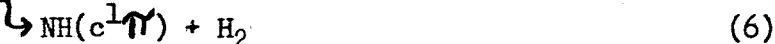
While all the results cannot be completely explained on the basis of any one primary process at the present time, the process



comes the closest to so doing and will therefore form the basis for our discussion. Process (1) would be expected to be followed by

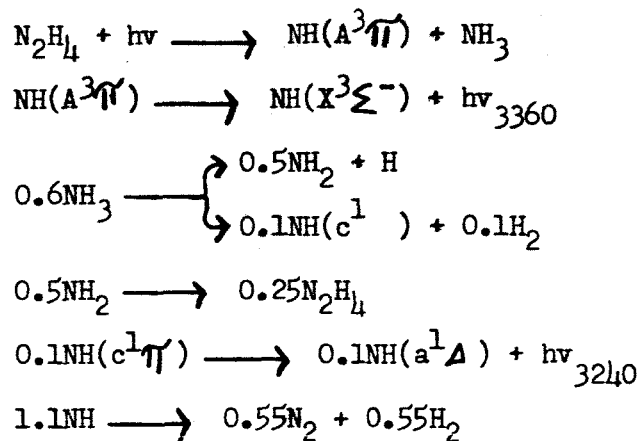


One would therefore expect $\phi_{-N_2H_4} = \phi_{NH_3} = 1$ and $\phi_{N_2} = \phi_{H_2} = 0.5$. It may be seen from the third column of table 1 that in photolysis at Kr lines for pressure in range 1-3 mm, this expectation is realized with the exception that $\phi_{H_2} = 1$. The low values for ϕ_{NH_3} and $\phi_{-N_2H_4}$ at 100u and the fact that the 3240\AA NH emission is observed after a few minutes photolysis suggest that photodecomposition of the ammonia product is occurring. McNesby, Tanaka and Okabe³ have shown that the following primary processes occur at the Kr lines

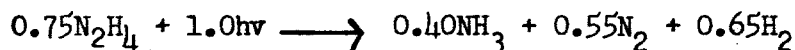


3. J. R. McNesby, I. Tanaka and H. Okabe, J. Chem. Phys. 36, 605 (1962).

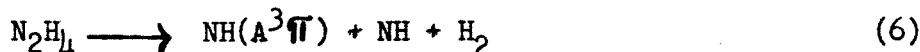
with process (6) being about 1/6 as probable as process (5). The formation of $\text{NH}(\text{c}^1\Pi)$ has been established by Becker and Welge^{1,2} in ammonia photolysis. Thus occurrence of (3) followed by partial photodecomposition of ammonia according to (5) and (6)



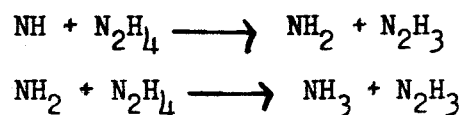
leads to the overall result



which is consistent with our observations. The decomposition of about 1/2 of the NH_3 formed initially (assuming $\phi_{\text{NH}_3} = 1$) is consistent with the duration of the experiments, the known intensity of the Kr lamp, the estimated effective concentration of NH_3 during photolysis and the known absorption coefficient of N_2H_4 ² ($381 \text{ cm}^{-1}\text{atm}^{-1}$) and NH_3 ⁴ ($400 \text{ cm}^{-1}\text{atm}^{-1}$). The occurrence² of



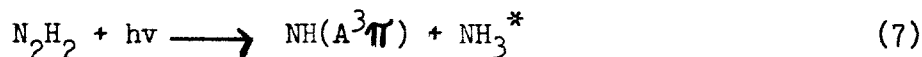
which is energetically possible at the 1236\AA Kr line, followed by



4. M. Zelikoff and K. Watanabe, J. Opt. Soc. Am. 43, 756 (1953).

would require $\phi_{-N_2H_4} = 3\phi_{NH_3}$ and that $\phi_{H_2} > \phi_{N_2}$. Our estimation that all these quantum yields are the same or nearly so indicates that the contribution of reaction (6) must be rather small. Other sequences involving secondary formation of NH_3 are subject to similar criticisms.

Our results at $100\mu N_2H_4$ and at the Kr lines could also be explained by formation of NH_3 with sufficient energy to decompose to $NH_2 + H$ if it is not quenched by collision with another molecule

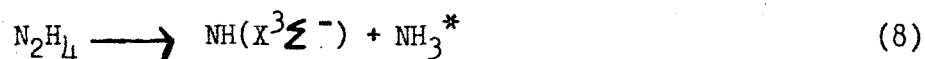


This however requires 104k.cal/mole over and above the 134k.cal/mole for reaction (3) or a total requirement of 238k.cal/mole. Since we have previously shown that the NH emission at 3360\AA is still produced when hydrazine is photolyzed using a Kr lamp with a CaF_2 window (eliminating the weaker 1165\AA line) the process producing $NH(A^3\Pi)$ must require 232k.cal/mole or less. Thus either (7) followed partially by



does not occur or the heats of formation used to estimate ΔH for reaction (7) and (7a) are off by at least 6k.cal/mole.

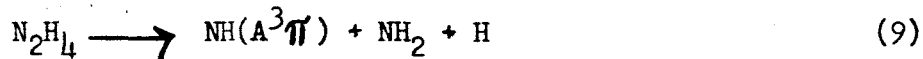
There is no apparent reason why process (3) which has a calculated $\Delta H = 134k.cal/mole$ should not occur at the Xe resonance line (1470\AA or $195k.cal/einstein$), unless all or most of the excess energy is not required to form ground state NH



is present as excitation energy in NH_3 . The excess energy in NH_3^* could be as high as 146k.cal/mole. Occurrence of process (8) with subsequent decomposition of NH_3^* would result in low values for ϕ_{NH_3}

and $\phi_{-N_2H_4}$ at low pressure and even at high pressure if NH_3^* is too short lived to be effectively quenched by collisions in the gas phase. This is what we observe qualitatively; there is a definite trend to higher values for ϕ_{NH_3} and $\phi_{-N_2H_4}$ with increasing pressure in photolysis at 1470\AA (table 2), and even in the millimeter region ϕ_{NH_3} is still less than 1.

More experiments will have to be performed before the importance of many of these processes can be determined. The effect of a high pressure of an inert gas would be of interest, especially at 1470\AA . The effect of a hydrogen atom scavenger such as C_2D_4 on the hydrogen production³ should be examined. Photolysis at other wavelengths would be significant since reaction (3) is energetically possible for wavelengths up to 2133\AA and the overall reaction (7 plus 7a)



is more likely to be energetically possible at Lyman- α (1216\AA or 235k.cal/einstein) than at 1236\AA .

2. PHOTON INDUCED CHEMICAL CONVERSION IN THE LOW TEMPERATURE METHANE HYDRATE $CH_4 \cdot 6H_2O$

2.1 Introduction

Previously we have observed that photolysis at the Kr resonance lines (1236\AA and 1165\AA) of $CH_4 \cdot 6H_2O$ results in the formation of H_2 , C_2H_6 , and CO_2 . Because of the unexpected CO_2 formation, great care was taken to ascertain that the starting materials were free from CO_2 contamination. However, because of the great potential significance of CO_2 formation upon irradiation of $CH_4 \cdot 6H_2O$ at -196°C ,

it was felt that an unequivocal demonstration was required of the fact that the water in the hydrate (rather than possible oxygen containing contaminants) was the source of CO_2 . Consequently, we have repeated the experiments using oxygen 18 water (90% H_2O^{18}). The formation of CO_2^{18} (mass 48 in a mass spectrometer) serves as evidence that CO_2 comes from water deposit. The experiments where mixtures of CH_4 and H_2O were photolyzed in the gas phase were also repeated since CO_2 has been observed as a product in these experiments as well.

The presence of CO as a product of the photolysis has been suspected in previous experiments, but identification was made difficult or impossible due to N_2 contamination in the CH_4 . Determination of CO in presence of N_2 requires that that mass ratio 28/14 in the mass spectrometer crocking pattern be accurately determined. The presence of a large excess of CH_4 (over 90% of sample after photolysis) and the contribution of CH_4 pattern to 16, 15 and 14 peaks precludes any such determination. However, the use of H_2O^{18} should result in the formation of CO^{18} appearing at mass 30 in the spectrometer and the presence of CO may then be directly established.

Finally, the gas phase photolysis of mixtures of C_2H_2 , C_2H_4 , and C_2H_6 with water have been examined for comparison with the CH_4 - H_2O system.

2.2 Results and Discussion

The photolysis of CH_4 - H_2O^{18} gaseous mixtures and the photolysis of the $\text{CH}_4 \cdot 6\text{H}_2\text{O}^{18}$ clathrate at -196°C both result in the formation of CO^{18} and CO_2^{18} as identified by masses 30 and 48

respectively in the mass spectrometer. Subsequent photolysis of $\text{CH}_4\text{-H}_2\text{O}^{16}$ in the same cell did not result in CO^{18} or CO_2^{18} formation, indicating that isotopic exchange was not occurring with water possibly absorbed in the system. The amount of CO^{18} , which can be directly determined from the size of the mass 30 peak, is comparable to the CO_2 formed in both the gas and solid phases. Precise determination of the amount of CO is not possible since it represents but a few percent of a large sample analyzed (90% CH_4 , remainder H_2 , N_2 , and CO).

The possible presence of other oxygenated compounds in the fraction removed at -80°C (mainly CO_2 and C_2H_6) is indicated by the fact that in the H_2O^{18} experiments, certain unexplained peaks appear at masses 29 to 32 whereas in the H_2O^{16} experiments, unaccounted for contributions to masses 28 and 29 are usually observed. This shift suggests that the ions in question contain oxygen. In the photolysis of gaseous mixtures of C_2H_2 and H_2O or C_2H_4 and H_2O , CO is a major product (along with hydrogen), but CO_2 is not formed. In the case of $\text{C}_2\text{H}_6\text{-H}_2\text{O}$, very small amounts of CO_2 have been observed. These results may have some bearing on the question as to whether or not CO is an intermediate in the formation of CO_2 .

3. PROTON BOMBARDMENT OF LOW TEMPERATURE SOLIDS

The proton source and associated gas handling system for low temperature solid studies (4°K — 90°K) has been completed. The system will provide for chemical analysis of the solid as well as emission and absorption studies. In addition simultaneous photon and or electron bombardment can be incorporated into the apparatus with only slight modification.

At the present time the system is being optimized for beam geometry, particle flux and energy range. Preliminary measurements indicate a proton-ion current of 5×10^{-6} amps at the ion bottle, using a biased faraday cup to eliminate secondary electrons. The ion source will initially provide a mixed beam of H_2^+ and H^+ ions. Later studies will be done with a magnetic analyzer to eliminate the H_2^+ ion.